

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) EP 0 646 630 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
23.04.1997 Bulletin 1997/17

(51) Int Cl.<sup>6</sup>: C09D 5/16, C09D 133/14,  
C09D 135/02, C09D 143/04

(21) Application number: 94115443.7

(22) Date of filing: 30.09.1994

(54) Antifouling coating composition

Anwuchsverhindernde Überzugszusammensetzung

Composition de revêtement anti-salissures

(84) Designated Contracting States:  
BE DE DK GB GR IT NL SE

(30) Priority: 30.09.1993 JP 269695/93

(43) Date of publication of application:  
05.04.1995 Bulletin 1995/14

(73) Proprietor: NOF CORPORATION  
Tokyo 100 (JP)

(72) Inventors:  
• Honda, Yoshihiro  
Kawanishi-shi, Hyogo (JP)  
• Masuoka, Shigeru  
Kobe-shi, Hyogo (JP)

• Itoh, Masayasu  
Itami-shi, Hyogo (JP)  
• Taniguchi, Masashige  
Tsukuba-shi, Ibaraki (JP)  
• Fukuda, Shigeo  
Nishinomiya-shi, Hyogo (JP)

(74) Representative:  
Hansen, Bernd, Dr. Dipl.-Chem. et al  
Hoffmann, Eitle & Partner,  
Patentanwälte,  
Arabellastrasse 4  
81925 München (DE)

(56) References cited:  
EP-A- 0 297 505 WO-A-84/02915  
GB-A- 2 255 343 US-A- 4 957 989

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 646 630 B1

## Description

FIELD OF THE INVENTION

5 The present invention relates to a coating composition for use in preventing the attachment of organisms to the surfaces of structures submerged in seawater.

BACKGROUND OF THE INVENTION

10 Antifouling paints employing an organotin copolymer and forming a coating film which gradually dissolves away in seawater are excellent in the ability to prevent the attachment of marine organisms to the surfaces of ship bottoms, etc., but the use thereof is restricted in recent years because of the problem of sea pollution.

As a coating composition for eliminating the sea pollution problem is widely used an antifouling paint employing rosin as a soluble resin. Antifouling paints employing polymers containing various hydrolyzable groups incorporated  
15 therein have also been proposed. However, these antifouling paints all have not been put to wide practical use. Among those antifouling paints is, for example, an antifouling paint of the hydrolyzable self-polishing type proposed in WO 84/02915 and JP-A-63-215780 which employs a (meth)acrylic ester polymer having triorganosilyl groups in side chains or a similar polymer. (The term "JP-A" as used herein means an "unexamined published Japanese patent application.")

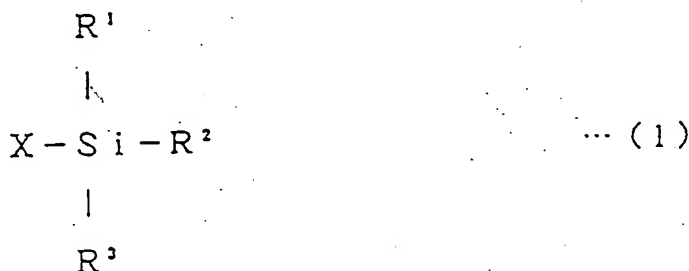
The present inventors made intensive studies on coating films of such an organosilicon-containing polymer. As a  
20 result, it was found that the antifouling paint employing a polymer modified by only incorporating triorganosilyl groups in side chains of the molecule as described in the above-cited reference has problems such as the following: (1) the coating film does not show erosion in the rotary test which is the most important test for evaluating hydrolyzable anti-  
fouling paints (a test for measuring coating film thickness reduction as erosion rate in which test pieces are fixed to the outer circumferential surface of a cylindrical drum and the drum is rotated in seawater at a peripheral speed of 16  
25 knots); (2) the coating film does not exhibit satisfactory antifouling properties in exposure test (immersion test); and (3) the coating film develops cracking and shows poor adherence to the substrate or primer coat, so that it peels off when immersed in seawater. Thus, the antifouling paints of the above-described kind do not have properties required for antifouling paints.

SUMMARY OF THE INVENTION

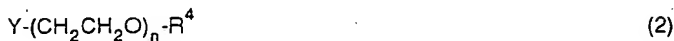
Accordingly, an object of the present invention is to provide a coating composition giving a coating film which  
undergoes neither cracking nor peeling and shows moderate hydrolyzability to dissolve into seawater constantly at an  
adequate rate and which therefore exhibits excellent antifouling property for long term.

35 As a result of intensive studies made by the present inventors in order to attain the above object, a specific copolymer has been invented. A specific copolymer in which alkoxy- or aryloxy polyethylene glycol groups as well as triorganosilyl groups have been incorporated into side chains of a molecule is used along with antifoulants to prepare a coating composition, this composition gives coating film which undergoes neither cracking nor peeling and shows moderate hydrolyzability to dissolve into seawater constantly at adequate rate and which exhibits excellent antifouling  
40 property for long term. The present invention has been completed based on the above astonishing finding.

The present invention is concerned with a coating composition containing as essential components antifoulants and copolymer obtained from monomers mixture comprising a monomer A represented by formula (1):



55 wherein R<sup>1</sup> to R<sup>3</sup> each is a group selected from alkyl groups and aryl groups and may be the same or different, and X is an acryloyloxy group, a methacryloyloxy group, a maleinoyloxy group, or a fumaroyloxy group and monomer B represented by formula (2):



wherein  $R^4$  is an alkyl group or an aryl group, Y is an acryloyloxy group, a methacryloyloxy group, a maleinoyloxy group, or a fumaroyloxy group, and n is an integer of 1 to 25.

#### DETAILED DESCRIPTION OF THE INVENTION

The coating composition of the present invention contains as one of its essential components copolymer obtained from monomers mixture which comprises at least one monomer A represented by the above-described formula (1) and at least one monomer B represented by the above-described formula (2) and which may optionally contain at least one monomer copolymerizable therewith (the copolymer is hereinafter referred to as "copolymer AB").

As shown in formula (1), monomer A has in its molecule an acryloyloxy group, a methacryloyloxy group, a maleinoyloxy group (mostly in the form of monoalkyl ester with 1-6 carbon atoms), or a fumaroyloxy group (mostly in the form of monoalkyl ester with 1-6 carbon atoms) as an unsaturated group (X) and also has a triorganosilyl group.

In the triorganosilyl group, the three alkyl or aryl groups ( $R^1$  to  $R^3$ ) may be the same or different. Specific examples of these groups include a linear or branched alkyl group having up to 20 carbon atoms (e.g., methyl, ethyl, propyl, and butyl); a cycloalkyl group (e.g., cyclohexyl and substituted cyclohexyl); and an aryl group (e.g., phenyl and naphthyl) and a substituted aryl group (e.g., substituted phenyl and substituted naphthyl). Examples of the substituted aryl groups include aryl groups substituted with a halogen atom, an alkyl group with up to about 18 carbon atoms, an acyl group, a nitro group, or an amino group.

Examples of monomer A which has a (meth)acryloyloxy group in a molecule include trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate, triisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-s-butylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, and tribenzylsilyl (meth)acrylate.

Other examples of monomer A having a (meth)acryloyloxy group in a molecule include ethyldimethylsilyl (meth)acrylate, n-butyldimethylsilyl (meth)acrylate, diisopropyl-n-butylsilyl (meth)acrylate, n-octyldi-n-butylsilyl (meth)acrylate, diisopropylstearyl silyl (meth)acrylate, dicyclohexylphenylsilyl (meth)acrylate, t-butyldiphenylsilyl (meth)acrylate, and lauryldiphenylsilyl (meth)acrylate.

Examples of monomer A which has a maleinoyloxy or fumaroyloxy group in a molecule include triisopropylsilyl methyl maleate, triisopropylsilyl amyl maleate, tri-n-butylsilyl n-butyl maleate, t-butyldiphenylsilyl methyl maleate, t-butyldiphenylsilyl n-butyl maleate, triisopropylsilyl methyl fumarate, triisopropylsilyl amyl fumarate, tri-n-butylsilyl n-butyl fumarate, t-butyldiphenylsilyl methyl fumarate, and t-butyldiphenylsilyl n-butyl fumarate.

As shown in formula (2), monomer B has in its molecule an acryloyloxy group, a methacryloyloxy group, a maleinoyloxy group (mostly in the form of monoalkyl ester with 1-6 carbon atoms), or a fumaroyloxy group (mostly in the form of monoalkyl ester with 1-6 carbon atoms) group as an unsaturated group (Y) and also has an alkoxy- or aryloxy-polyethylene glycol group.

In the alkoxy- or aryloxy-polyethylene glycol group, the degree of polymerization (n) of the polyethylene glycol is from 1 to 25. Examples of the alkyl or aryl group ( $R^4$ ) include a linear or branched alkyl group having up to 12 carbon atoms (e.g., methyl, ethyl, propyl, and butyl); a cycloalkyl group (e.g., cyclohexyl and substituted cyclohexyl); and an aryl group (e.g., phenyl and naphthyl) and a substituted aryl group (e.g., substituted phenyl and substituted naphthyl). Examples of the substituted aryl groups include aryl groups substituted with a halogen atom, an alkyl group with up to about 18 carbon atoms, an acyl group, a nitro group, or an amino group.

Examples of monomer B which has a (meth)acryloyloxy group in a molecule include methoxyethyl (meth)acrylate, ethoxyethyl (meth)acrylate, propoxyethyl (meth)acrylate, butoxyethyl (meth)acrylate, hexoxyethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, methoxytriethylene glycol (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, and ethoxytriethylene glycol (meth)acrylate.

Examples of monomer B which has a maleinoyloxy or fumaroyloxy group in a molecule include methoxyethyl n-butyl maleate, ethoxydiethylene glycol methyl maleate, ethoxytriethylene glycol methyl maleate, propoxydiethylene glycol methyl maleate, butoxyethyl methyl maleate, hexoxyethyl methyl maleate, methoxyethyl n-butyl fumarate, ethoxydiethylene glycol methyl fumarate, ethoxytriethylene glycol methyl fumarate, propoxydiethylene glycol methyl fumarate, butoxyethyl methyl fumarate, and hexoxyethyl methyl fumarate.

As other monomers copolymerizable with these monomers A and B, use may be made of various vinyl monomers such as acrylic esters, methacrylic esters, styrene, vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate), vinyltoluene,  $\alpha$ -methylstyrene, crotonic esters, and itaconic esters.

In the monomers mixture, the proportions of monomers A and B and other monomer(s) copolymerizable therewith

may be suitably determined depending on the use of the coating composition. In general, however, it is preferred that the proportion of monomer A is from 1 to 95% by weight, that of monomer B is from 1 to 95% by weight, and that of other monomer(s) copolymerizable therewith is from 0 to 95% by weight on the basis of the total weight of the monomers.

5 Copolymer AB can be obtained by polymerizing such monomers mixture in the presence of a vinyl polymerization initiator by any of various methods such as solution polymerization, bulk polymerization, emulsion polymerization, and suspension polymerization in an ordinary way. In preparing a coating composition from copolymer AB, it is advantageous to dilute the copolymer with an organic solvent to give a polymer solution having an adequate viscosity. For this, it is desirable to employ the solution polymerization method or bulk polymerization method.

10 Examples of the vinyl polymerization initiator include azo compounds such as azobisisobutyronitrile and triphenylmethylazobenzene; and peroxides such as benzoyl peroxide, di-t-butyl peroxide, t-butyl peroxybenzoate, and t-butyl peroxyisopropylcarbonate.

15 Examples of the organic solvent include aromatic hydrocarbons such as xylene and toluene; aliphatic hydrocarbons such as hexane and heptane; esters such as ethyl acetate and butyl acetate; alcohols such as isopropyl alcohol and butyl alcohol; ethers such as dioxane and diethyl ether; and ketones such as methyl ethyl ketone and methyl isobutyl ketone. The solvents are used either alone or in combination.

20 The molecular weight of copolymer AB thus obtained is desirably in the range of from 1,000 to 150,000 in terms of weight-average molecular weight. Too low molecular weights result in difficulties in forming normal coating film, while too high molecular weights result in disadvantages that a single coating operation only gives thin coating film and, hence, coating operations should be conducted in a larger number. It is advantageous that the viscosity of the solution of copolymer AB is 150 P or lower at 25°C. For attaining this, it is preferred to regulate the solid content of the polymer solution to a value in the range of from 5 to 90% by weight, desirably from 15 to 85% by weight.

25 The antifoulant used as another essential component in the coating composition of the present invention may be any of a wide range of conventionally known antifoulants. The known antifoulants are roughly divided into inorganic compounds, metal-containing organic compounds, and metal-free organic compounds.

Examples of the inorganic compounds include copper compounds such as cuprous oxide, copper powder, copper thiocyanate, copper carbonate, copper chloride, and copper sulfate, zinc sulfate, zinc oxide, nickel sulfate, and copper-nickel alloys.

30 Examples of the metal-containing organic compounds include organocopper compounds, organonickel compounds, and organozinc compounds. Also usable are maneb, manzeb, propineb, and the like. Examples of the organocopper compounds include oxine copper, copper nonylphenolsulfonate, copper bis(ethylenediamine) bis(dodecylbenzenesulfonate), copper acetate, copper naphthenate, and copper bis(pentachlorophenolate). Examples of the organonickel compounds include nickel acetate and nickel dimethyldithiocarbamate. Examples of the organozinc compounds include zinc acetate, zinc carbamate, zinc dimethyldithiocarbamate, zinc pyrrithione, and zinc ethylenebis(dithiocarbamate).

35 Examples of the metal-free organic compounds include N-trihalomethylthiophthalimides, dithiocarbamic acids, N-arylmaleimides, 3-(substituted amino)-1,3-thiazolidine-2,4-diones, dithiocyano compounds, triazine compounds, and others.

40 Examples of the N-trihalomethylthiophthalimides include N-trichloromethylthiophthalimide and N-fluorodichloromethylthiophthalimide. Examples of the dithiocarbamic acids include bis(dimethylthiocarbamoyl) disulfide, ammonium N-methyldithiocarbamate, ammonium ethylenebis(dithiocarbamate), and milneb.

Examples of the N-arylmaleimides include N-(2,4,6-trichlorophenyl)maleimide, N-4-tolylmaleimide, N-3-chlorophenylmaleimide, N-(4-n-butylphenyl)maleimide, N-(anilinophenyl)maleimide, and N-(2,3-xylyl)maleimide.

45 Examples of the 3-(substituted amino)-1,3-thiazolidine-2,4-diones include 3-benzylideneamino-1,3-thiazolidine-2,4-dione, 3-(4-methylbenzylideneamino)-1,3-thiazolidine-2,4-dione, 3-(2-hydroxybenzylideneamino)-1,3-thiazolidine-2,4-dione, 3-(4-dimethylaminobenzylideneamino)-1,3-thiazolidine-2,4-dione, and dimethylaminobenzylideneamino-1,3-thiazolidine-2,4-dione, and 3-(2,4-dichlorobenzylideneamino)-1,3-thiazolidine-2,4-dione.

Examples of the dithiocyano compounds include dithiocyanomethane, dithiocyanoethane, and 2,5-dithiocyanophene. Examples of the triazine compounds include 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine.

50 Other examples of the metal-free organic compounds include 2,4,5,6-tetrachloroisophthalonitrile, N,N-dimethyldichlorophenylurea, 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one, N,N-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfamide, tetramethylthiuram disulfide, 3-iodo-2-propylbutyl carbamate, 2-(methoxycarbonylamino)benzimidazole, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, diiodomethyl-p-tolyl sulfone, bis(dimethylcarbamoyl)zinc ethylene bis(dithiocarbamate), phenyl(bispyridine)bismuth dichloride, 2-(4-thiazolyl)benzimidazole, and pyridine triphenylborane.

55 One or more antifoulants selected from such antifoulants are employed in the present invention. The antifoulants are used in such an amount that the proportion thereof in the solid contents of the coating composition is usually from 0.1 to 80% by weight, preferably from 1 to 60% by weight. Too small antifoulant amounts do not produce an antifouling effect, while too large antifoulant amounts result in the formation of a coating film which is apt to develop defects such

as cracking and peeling and thus becomes less effective in antifouling property.

Additive ingredients may optionally be incorporated into the coating composition of the present invention thus prepared. Examples of the additive ingredients are colorants such as pigments (e.g., red iron oxide, zinc oxide, titanium dioxide, talc), and dyes, dehumidifiers, and additives ordinarily employed in coating compositions as antisagging agents, antiflooding agents, antisetling agents, and antifoaming agents.

For formulating antifouling coating film from the coating composition of the present invention on the surface of a structure to be submerged in seawater, use may be made of a method in which the coating composition is applied on the surface in a suitable manner and the solvent is removed by evaporation at ordinary temperature or with heating. By this method, a dry coating film can be easily formed on the surface of the structure.

The coating composition of the present invention is applicable to objects required to be protected against the fouling or damage caused by marine organisms, such as ship bottoms, fishing nets, and underwater structures including cooling water pipes, and is also usable for the prevention of sludge diffusion in marine construction works. In such applications, the coating film undergoes neither cracking nor peeling, shows moderate hydrolyzability to dissolve into the seawater constantly at adequate rate, and is hence capable of affording long-lasting excellent protection against the fouling or damage caused by marine organism attachment.

The present invention will be explained below in more detail by reference to preparation examples, examples (of the present invention), and comparative examples. In these examples, unless otherwise indicated, all parts are by weight and the molecular weights are given in terms of weight-average molecular weight measured by GPC and calculated for standard polystyrene. Monomers A ( $A_1$  to  $A_7$ ) used in the preparation examples are those represented by the above-described formula (1), with the  $R^1$  to  $R^3$  and X in the formula being specified in Table 1 given below. Further, monomers B ( $B_1$  to  $B_7$ ) used in the preparation examples are those represented by the above-described formula (2), with the Y, n, and  $R^4$  in the formula being specified in Table 2 given below.

Table 1

	Organic Groups in General Formula (1)			
	$R^1$	$R^2$	$R^3$	X
Monomer $A_1$	$CH_3$	$CH_3$	$t-C_4H_9$	$CH_2=CHCOO$
Monomer $A_2$	$i-C_3H_7$	$i-C_3H_7$	$i-C_3H_7$	$CH_2=CHCOO$
Monomer $A_3$	$n-C_4H_9$	$n-C_4H_9$	$n-C_4H_9$	$CH_2=C(CH_3)COO$
Monomer $A_4$	$C_6H_5$	$C_6H_5$	$t-C_4H_9$	$CH_2=C(CH_3)COO$
Monomer $A_5$	$i-C_3H_7$	$i-C_3H_7$	$i-C_3H_7$	$CH_2=C(CH_3)COO$
Monomer $A_6$	$C_6H_5$	$C_6H_5$	$t-C_4H_9$	$C_5H_{11}OOCCH=CHCOO$ (maleinoyloxy group)
Monomer $A_7$	$n-C_4H_9$	$n-C_4H_9$	$n-C_4H_9$	$C_5H_{11}OOCCH=CHCOO$ (fumaroyloxy group)

Table 2

	Organic Groups in General Formula (2)		
	Y	n	$R^4$
Monomer $B_1$	$CH_2=CHCOO$	1	$CH_3$
Monomer $B_2$	$CH_2=C(CH_3)COO$	1	$CH_3$
Monomer $B_3$	$CH_2=CHCOO$	2	$C_2H_5$
Monomer $B_4$	$CH_2=C(CH_3)COO$	9	$C_6H_5$
Monomer $B_5$	$CH_2=C(CH_3)COO$	23	$C_4H_9$
Monomer $B_6$	$C_4H_9OOCCH=CHCOO$ (maleinoyloxy group)	1	$CH_3$
Monomer $B_7$	$CH_3OOCCH=CHCOO$ (fumaroyloxy group)	2	$C_2H_5$

#### PREPARATION EXAMPLES 1 TO 5

According to the formulations shown in Table 3 given below, solvent a was placed in a flask equipped with a stirrer and heated to a predetermined reaction temperature, following which a liquid mixture consisting of monomer A, monomer B, other monomers, and a polymerization catalyst a was introduced dropwise into the flask with stirring over a period of 3 hours. After completion of the addition, the contents were held at that temperature for 30 minutes. A mixture of a solvent b and a polymerization catalyst b was then added dropwise over a period of 20 minutes, and the resulting mixture was stirred at that temperature for 2 hours to complete the polymerization reaction. Finally, a diluent solvent

was added to dilute the reaction mixture. Thus, polymer solutions S<sub>1</sub> to S<sub>5</sub> were obtained.

In Table 3, "Perbutyl I" (trade name of NOF Corporation, Japan) given as a polymerization catalyst is t-butyl peroxyisopropylcarbonate.

Table 3

Formulation Solvent a (parts)	Preparation Example				
	1	2	3	4	5
Xylene	40	40	-	30	40
Butyl acetate	-	10	40	-	-
Monomer A <sub>1</sub>	5	-	-	-	-
Monomer A <sub>2</sub>	-	60	-	-	-
Monomer A <sub>3</sub>	-	-	55	-	-
Monomer A <sub>4</sub>	45	-	-	50	-
Monomer A <sub>5</sub>	-	-	-	-	30
Monomer A <sub>6</sub>	-	-	-	-	-
Monomer A <sub>7</sub>	-	-	-	-	-
Monomer B <sub>1</sub>	10	-	-	-	40
Monomer B <sub>2</sub>	-	15	-	-	-
Monomer B <sub>3</sub>	-	-	15	-	-
Monomer B <sub>4</sub>	-	-	5	-	30
Monomer B <sub>5</sub>	-	-	-	10	-
Monomer B <sub>6</sub>	-	-	-	-	-
Monomer B <sub>7</sub>	-	-	-	-	-

Table 3 (cont'd)

Formulation (parts)	Other monomers	Preparation Example				
		1	2	3	4	5
	Methyl methacrylate	35	20	20	30	-
	n-Butyl methacrylate	-	5	-	-	-
	n-Butyl acrylate	-	-	5	-	-
	Octyl acrylate	-	-	-	10	-
	Vinyl acetate	-	-	-	-	-
	Styrene	5	-	-	-	-
	Polymerization Azobisisobutyronitrile	-	-	-	-	1
	catalyst <u>a</u>	2	1	2	5	-
	Solvent <u>b</u>	10	10	10	10	10
	Polymerization Azobisisobutyronitrile	-	-	-	-	1
	catalyst <u>b</u>	1	1	1	1	-
	Diluent	47	48	16	54	48
	solvent	-	-	31	-	-
	Reaction Temperature (°C)	140	134	142	118	80
	Solid Content (%)	50	50	50	50	50
	Molecular Weight of the Polymer (x1000)	31	28	67	3	40
	Polymer Solution	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	S <sub>5</sub>

## PREPARATION EXAMPLE 6

In a heat- and pressure-resistant vessel were placed monomer A, monomer B, other monomers, and polymerization catalyst a according to the formulation shown in Table 4 given below. The vessel was completely sealed. The contents were then heated to a predetermined reaction temperature with shaking and the shaking was continued at that temperature for 8 hours to complete the reaction. A diluent solvent was then added to dissolve the reaction product with shaking for 1 hour, thereby giving a polymer solution S<sub>6</sub>. In Table 4, "Perbutyl I" given as a polymerization catalyst has the same meaning as in Table 3.

